

Fénnyel indukált ultragyors dinamikai folyamatok molekuláris rendszerekben

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Overview

- 1 Conical intersections
- 2 Light-induced conical intersections (LICI)
- 3 Topological or Berry phase (BF)
- 4 Wave packet dynamics
- 5 Photodissociation dynamics of the D_2^+ molecule
- 6 Experiment
- 7 First direct result
- 8 Summary and outlook

Born-Oppenheimer adiabatikus közelítés

Egyik fontos alapkötét adja a molekulafizikai és kémiai folyamatok leírásának. Számos kémiai folyamat leírható segítségével. (Amikor az atommagok dinamikája egyetlen Born-Oppenheimer potenciális energia felületen írható le.)

- Adott elektronállapotú molekula rezgések normálmodosulású leírása
- Több atomos molekulák gerjesztett vibrációs szintjeinek lebomlása
- Atom-molekula ütközések reakció hatáskeresztmetszetének számítása stb...

A nemadiabatikus folyamatok

Ekkor az atommagok dinamikáját már legalább 2, vagy több csatolt B-O potenciális energia felületen írhatjuk le (nem vizsgálhatók a Born-Oppenheimer adiabatikus közelítés keretein belül).

Ide tartoznak:

- Fotokémiai, fotobiológiai folyamatok
- Gerjesztett elektronállapotok sugárzás mentes relaxációs folyamatai
- Több atomos molekulák izomerizációs folyamatai
- Foton indukált unimolekuláris lebomlások stb.

Nemadiabatikus folyamatok

Vizsgálatukban (kísérlet, elmélet) és értelmezésükben az utóbbi néhány évtizedben rohamos változás következett be.

- 1. A femto-sec. laser technológiák, és „time-resolved” spektroszkópiai módszerek elterjedése. (Gerjesztett elektron állapotok sugárzásmentes lebomlása sokkal gyorsabban történik, mint ahogy azt korábban gondolták.)
A hagyományos elméletek a gerjesztett elektronállapotok sugárzásmentes lebomlására (60-as 70-es évek) nem tudták a femto-sec. időskálát megmagyarázni!!!

Nemadiabatikus folyamatok

- 2. A „multi-reference” típusú elektronszerkezet módszerek széleskörű elterjedése. Rámutattak arra, hogy a többatomos molekulák multidimenziós hiperfelületei között (alap és gerjesztett állapotok) megjelenő ú.n. kónikus kereszteződések („conical intersection” ,CI, 1929 Neumann János és Wigner Jenő megjósolták) szinte minden jelen vannak és szerepük óriási. A CI-k igazi jelentősége csak mostanában válik igazán ismertté. CI-ken keresztül játszódnak le a nagyon gyors, sugárzás nélkül végbemenő folyamatok („ultrafast radiationless decay”), ahogyan azt 1937-ben Teller Ede megjósolta.

Nemadiabatikus folyamatok

- Habár a Cl maga egy elméleti fogalom, és mint olyan kísérletileg közvetlenül nem mutatható ki, de a segítségükkel kifejlesztett elméleti eljárások és módszerek alkalmasak arra, hogy kísérletek eredményeit jósolják meg, vagy megmagyarázzák azokat.

Born-Oppenheimer adiabatikus és a nemadiabatikus közelítés

A teljes molekuláris Hamilton operátor:

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{U}(\vec{r}, \vec{R})$$

ahol $\hat{T}_e \doteq$ elektron kinetikus energia

$\hat{T}_N \doteq$ mag kinetikus energia

$$\hat{U}(\vec{r}, \vec{R}) = \hat{U}_{ee}(\vec{r}) + \hat{U}_{eN}(\vec{r}, \vec{R}) + \hat{U}_{NN}(\vec{R})$$

$\vec{r} \doteq$ elektron koordináták

$\vec{R} \doteq$ mag koordináták

Born–Oppenheimer adiabatikus és a nemadiabatikus közelítés

Ha $\hat{T}_N = 0$, vagyis $\hat{H} = \hat{T}_e + \hat{U}(\vec{r}, \vec{R}) = \hat{H}_e \implies$ az elektronok mozgását írjuk le rögzített magok mellett, azaz

$$[\hat{H}_e - V_n(\vec{R})] \Phi_n(\vec{r}, \vec{R}) = 0$$

(A mag koordináták csak paraméterek!)

$\Phi_n(\vec{r}, \vec{R}) \doteq$ Born–Oppenheimer elektron állapot

$V_n(\vec{R}) \doteq$ Born–Oppenheimer potenciális energiafelület

Born–Oppenheimer adiabatikus és a nemadiabatikus közelítés

A rendszer egzakt sajátállapotai sorbafejthetők a Born–Oppenheimer elektronállapotok szerint:

$$\Psi(\vec{r}, \vec{R}) = \sum_n \chi_n(\vec{R}) \Phi_n(\vec{r}, \vec{R})$$

Ezt beírva a Scrödinger–egyenletbe $([\hat{H} - E] \Psi(\vec{r}, \vec{R})) = 0$ kapjuk:

$$[\hat{T}_N + \hat{V}_n(\vec{R}) - E] \chi_n(\vec{R}) = \sum_m \hat{\Lambda}_{nm} \chi_m(\vec{R}) \quad *$$

ahol $\hat{\Lambda}_{nm}$ a nemadiabatikus csatolások operátora:

$$\hat{\Lambda}_{nm} = \sum_{i=1}^M \hat{F}_{nm}^{(i)} \frac{\partial}{\partial R_i} - \hat{G}_{nm}.$$

Itt $\hat{F}_{nm}^{(i)} = 2 \sum_{j=1}^M \int d\vec{r} \Phi_n^* \alpha_{ij} \frac{\partial \Phi_m}{\partial R_j}$ és $\hat{G}_{nm} = \int d\vec{r} \Phi_n^* (\hat{T}_N \Phi_m)$.

Ha a * egyenlet J.O.=0 \implies Born–Oppenheimer adiabatikus közelítés.

(Itt feltételezzük, hogy a mag kinetikus energia operátor csak kis perturbációt jelent az elektronmozgásában. Jó közelítés, ha az egyes elektronállapotok energiái nincsenek túl közel egymáshoz.)

$$\Psi(\vec{r}, \vec{R}) = \chi_n \Phi_n(\vec{r}, \vec{R})$$

A Born–Oppenheimer adiabatikus közelítés érvényét veszíti, ha a különböző elektronállapotok potenciális energiafelületei közel kerülnek egymáshoz. (Az egyes elektronállapotokat a mag mozgás csatolja.) Ekkor legalább kettő, vagy több állapotot kell figyelembe venni!

$$\left[\hat{T}_N + \hat{V}_n(\vec{R}) - E \right] \chi_n(\vec{R}) = \sum_m \hat{\Lambda}_{nm} \chi_m(\vec{R})$$

$\hat{\Lambda}$ nemadiabatikus csatolási operátor nem hanyagolható el!
Átalakítva momentum csatolássá (mátrixegyenlet):

$$-\frac{1}{2M} (\Delta + \tau)^2 \Psi + (V - E) \Psi = 0$$

$$\tau_{nm} = \int d\vec{r} \Phi_n^* \frac{\partial}{\partial R_i} \Phi_m \sim \frac{1}{V_{nn} - V_{mm}}. \quad V \text{ diagonális mátrix}$$

Elfajult állapotok esetén: $\tau \rightarrow \infty$, szingularitás, numerikusan kezelhetetlen.

Megoldás: „diabatizálás”, potenciál csatolás $-\frac{1}{2M} \Delta^2 \Psi + (W - E) \Psi = 0$.

W már nem diagonális, ide transzformáltuk a csatolást.

Két–atomos molekulák: non–crossing rule;

De három atomos rendszerekben léteznek elfajulások, CI-k.

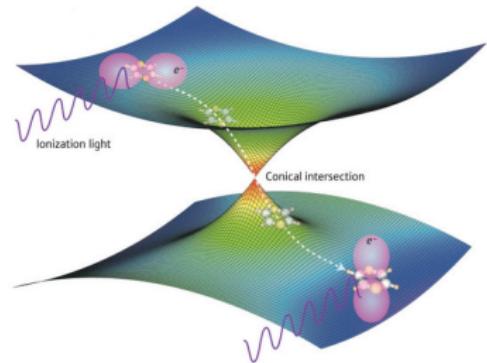
Az atomok számának növekedésével rohamosan nő a CI-k száma is.

Nagy biomolekulák esetén CI-k száma „ ∞ ”.

A CI-k „fotokémiai csatornaként” szolgálnak a gerjesztett állapotok ultragyors (femto-sec. időskála) lebomlásához.

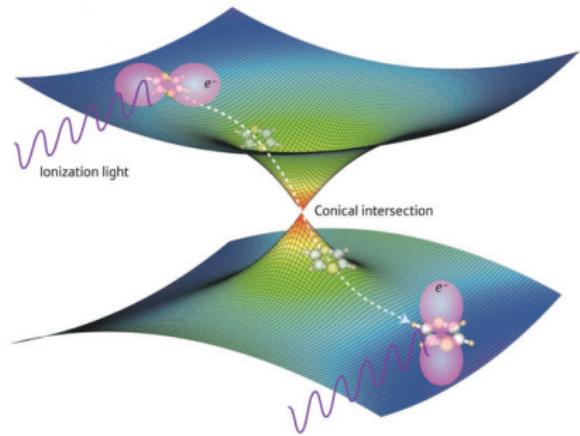
Conical Intersections

- Conical intersections (CIs) play an important role in nonadiabatic processes such as
 - **dissociation**
 - **radiationless relaxation** of excited states
 - **proton transfer**
 - **isomerization** processes of polyatomics
 - etc...

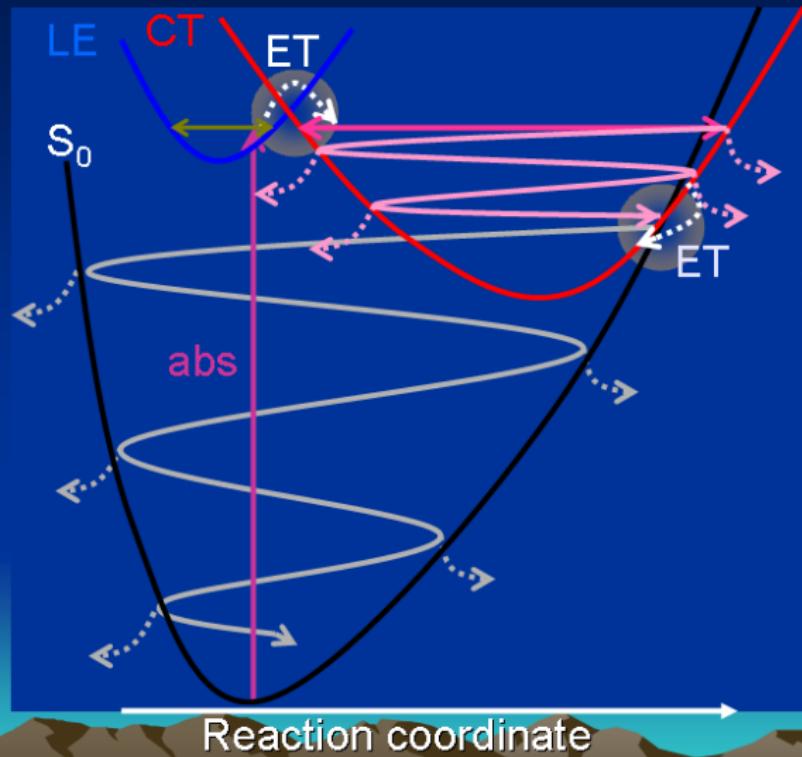


Conical Intersections

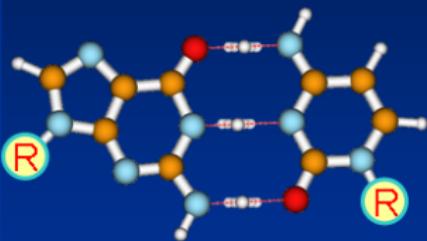
- Cls affect other important processes as well, such as
 - **photosynthesis** in plants
 - **photochemistry** of DNA
 - **fluorescence** of proteins
 - **molecular electronics**
 - etc...



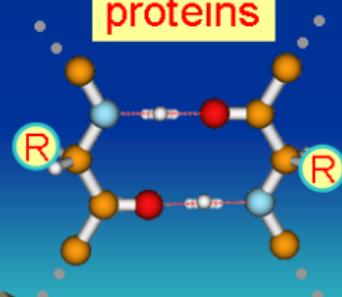
Internal Conversion via Electron-Driven Proton-Transfer (EDPT) process



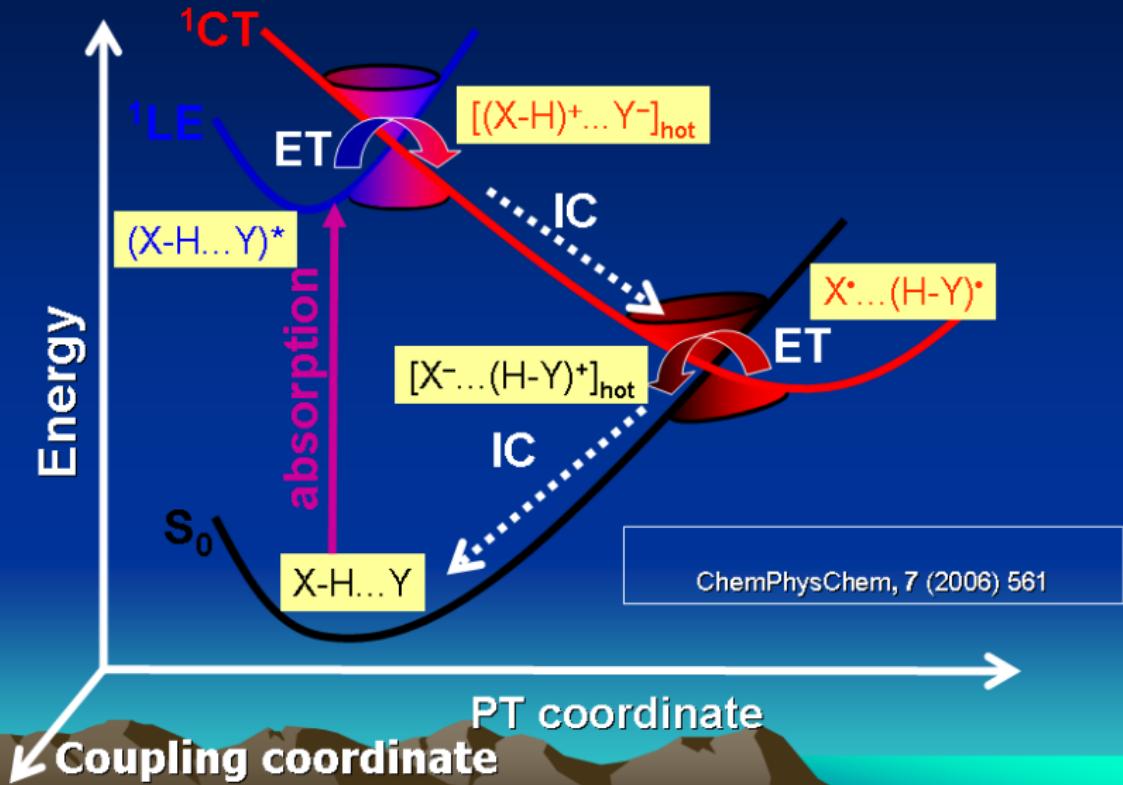
DNA



proteins

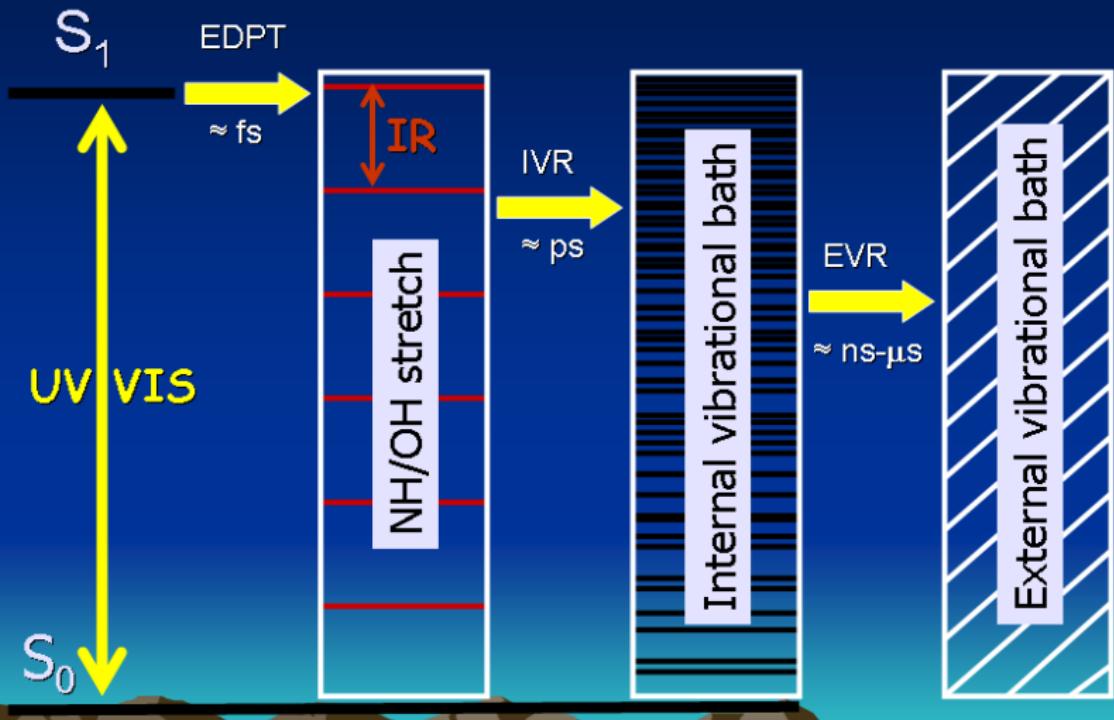


Internal Conversion via Electron-Driven Proton-Transfer (EDPT) process



ChemPhysChem, 7 (2006) 561

Photostability via EDPT process



Conical Intersections

- It is well known that **Conical Intersections (CIs) cannot be formed** in field-free diatomics.
- **But**, by applying external electric fields, CIs can be created even in diatomics.
- In this situation the **laser light induces CIs (LICIs)** which **couple** the **electronic states** and the internal **rotational** and **vibrational** motions.

Light Induced Conical Intersections (LICI)

The Hamiltonian of a diatomic molecule in a linearly polarized laser wave given by formula

$$\mathbf{H}(t) = \hat{T}_{R,\Theta,\Phi} + \mathbf{H}_{el}(R) + \varepsilon_0 \cos(\omega_L t) \sum_j (z_j \cos \Theta + x_j \sin \Theta)$$

The ω_L laser frequency can couple two electronic states ($|\psi_1^e\rangle, |\psi_2^e\rangle$) of the molecule by single photon excitation.

For the case of $N\alpha_2$ molecule ($X^1\Sigma_g^+$ and $A^1\Sigma_g^+$, $\lambda = 667\text{nm}$).

Due to symmetry, the only non-vanishing dipole matrix element responsible for light-induced electronic transitions is $d(R) = \langle \psi_1^e | \sum_j z_j | \psi_2^e \rangle$.

N. Moiseyev, M. Sindelka and L.S. Cederbaum, *J. Phys. B*: 41 (2008) 221001.

M. Sindelka, N. Moiseyev and L.S. Cederbaum, *J. Phys. B*: 44 (2011) 045603.

Light Induced Conical Intersections (LICI)

In the space of the two electronic states the static, dressed state representation (Floquet representation) form of this Hamiltonian is the following:

$$\begin{aligned}\mathbf{H} = & \left(-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\mathbf{L}_{\theta\varphi}^2}{2\mu R^2} \right) \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ & + \begin{pmatrix} V_X(R) & (\mathcal{E}_0/2) d(R) \cos \theta \\ (\mathcal{E}_0/2) d(R) \cos \theta & V_A(R) - \hbar\omega_L \end{pmatrix}\end{aligned}$$

Let us diagonalize the potential matrix to obtain the two adiabatic (BO) PES ($V_{ad}^{lower}(R, \theta); V_{ad}^{upper}(R, \theta)$). One can obtain CI only if the **two conditions** $\cos \theta = 0$, ($\theta = \pi/2$) and $V_X(R) = V_A(R) - \hbar\omega_L$ are simultaneously fulfilled.

Light Induced Conical Intersections (LICI)

- The laser induced CI leads to a breakdown of the B-O picture of single surface dynamics.
- Let us diagonalize the potential matrix and thus transform \hat{H} to the adiabatic representation:

$$\hat{U}(R, \theta) = \begin{pmatrix} \cos \Phi(R, \theta) & \sin \Phi(R, \theta) \\ -\sin \Phi(R, \theta) & \cos \Phi(R, \theta) \end{pmatrix}$$

where

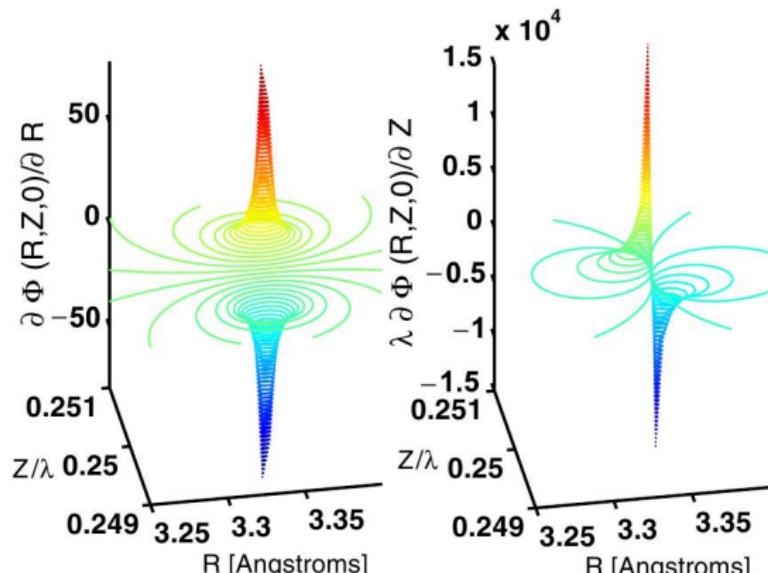
$$\Phi(R, \theta) = \frac{1}{2} \arctan \left(\frac{\varepsilon_0 d(R) \cos \theta}{E_A(R) - \hbar \omega_L - E_x(R)} \right).$$

Light Induced Conical Intersections (LICI)

In this representation $\hat{U}\hat{H}\hat{U}^\dagger$ gives the **adiabatic PES**

($V_{ad}^{upper}(R, \theta)$; $V_{ad}^{lower}(R, \theta)$) and the kinetic energy operator contains the nonadiabatic couplings.

Light induced CIs introduce infinitely strong nonadiabatic coupling!



Topological or Berry phase (BF)

- It is known that each real adiabatic electronic state **changes sign** when transported continuously along a closed loop enclosing the point of CI.
- As the total wave function must be single valued one has to multiply it by a phase factor ensuring that the total wave function remains **single valued**.
- This modification has a **direct effect** on the nuclear dynamics.
- Consequently, the **appearance of the BF** in a molecular system can be considered as a **clear signature of the CI** independently of whether it is natural or a laser induced one.

G. Herzberg and H.C. Longuet-Higgins, *Diss. Faraday. Soc.*: 35 (1963) 77.

M. V. Berry: *Proc. R. Soc. A*: 392 (1984) 45.

Topological or Berry phase (BF)

It is known that the topological or BF α_{12} can be calculated for a closed contour Γ as

$$\alpha_{12} = \oint_{\Gamma} \tau_{12}(s') \cdot ds',$$

where τ_{12} is the nonadiabatic coupling term between the two electronic states.

It is also known that

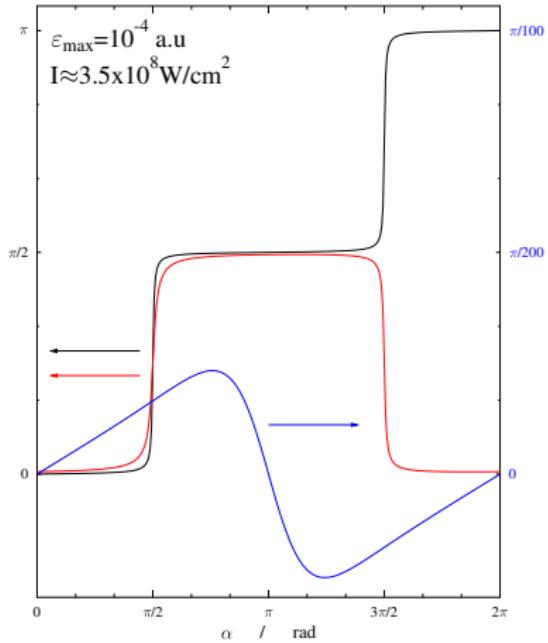
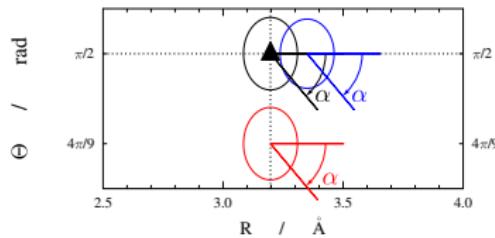
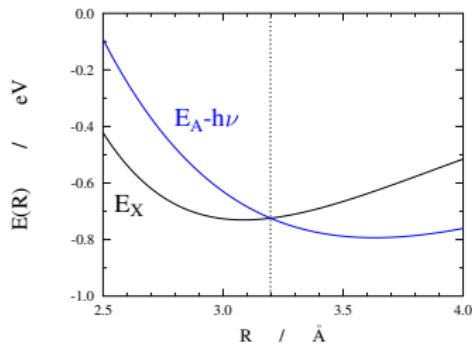
$$\alpha_{12} = \pi \begin{cases} 2n + 1 & \Gamma \text{ encircles odd number of Cls} \\ 2n & \Gamma \text{ encircles even number of Cls} \end{cases} \quad n = 0, \pm 1, \pm 2, \dots$$

In our case it is easy to see that

$$\alpha_{12} = \Phi_{end}(R, \Theta) - \Phi_{begin}(R, \Theta).$$

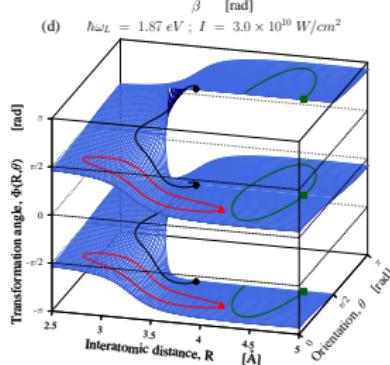
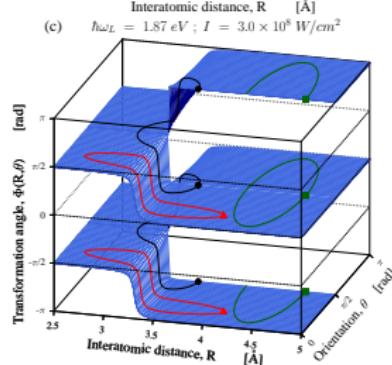
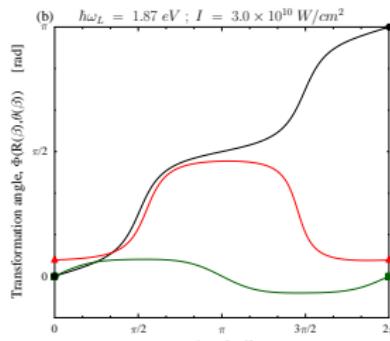
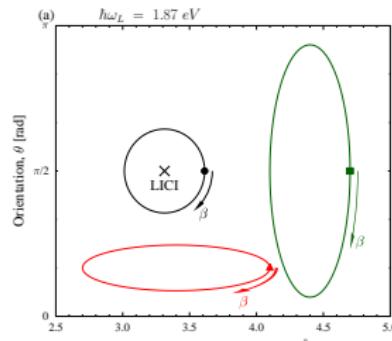
M. Baer, *Chem. Phys. Lett.* 35 (1975) 112; M. Baer, A. Alijah, *Chem. Phys. Lett.* 319 (2000) 489; M. Baer, *Chem. Phys.* 259 (2000) 123.

Topological or Berry phase (BF)



G. J. Halász, Á. Vibók, M. Sindelka, N. Moiseyev and L.S. Cederbaum, *J. Phys. B*: **44**, 175102, (2011).

Topological or Berry phase (BF)



G. J. Halász, M. Sindelka, N. Moiseyev, L.S. Cederbaum and Á. Vibók, *J. Chem. Phys. A.*: **116**, 2636, (2012).

Wave packet Dynamics

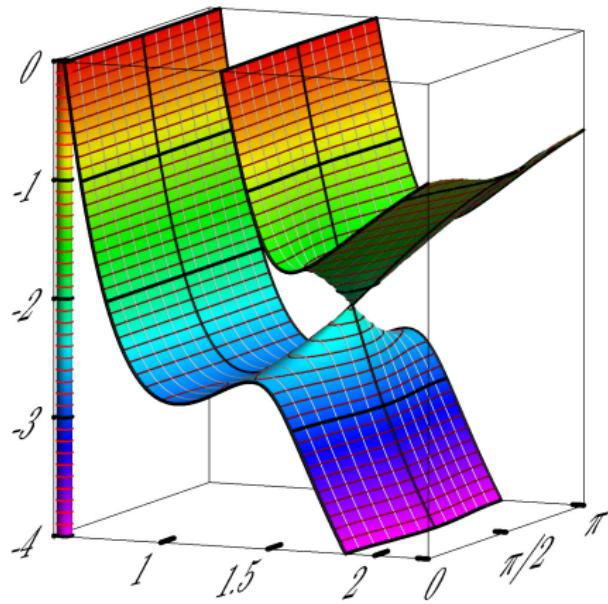
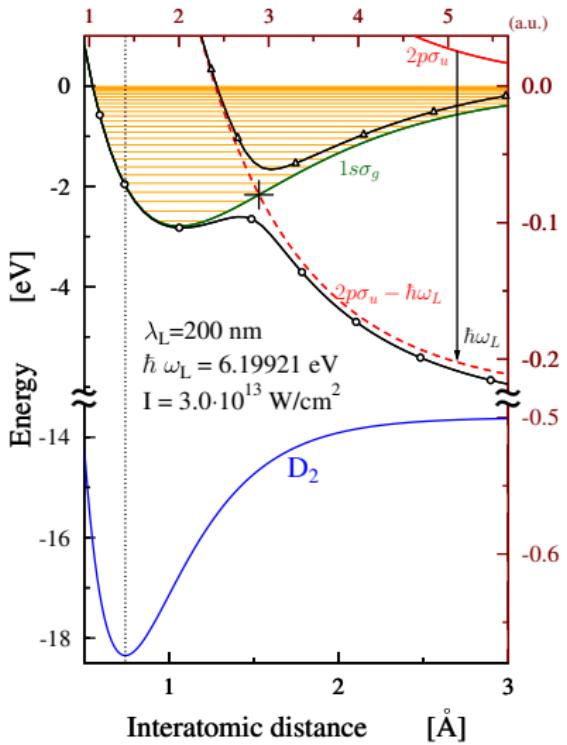
The MCTDH method is used to solve the TD nuclear Schrödinger equations

$$i\dot{\Psi}(t) = \hat{H}(t)\Psi(t) = [\hat{T}_{nuc} + \hat{H}_{el} + \hat{d} \cdot E(t)] \Psi(t)$$

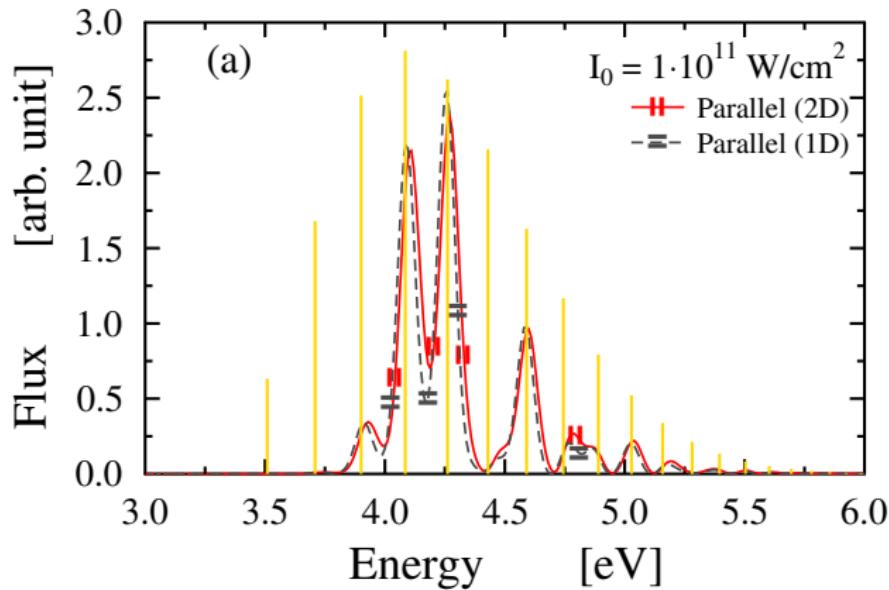
($e = m_e = \hbar = 1$; atomic units).

- Floquet Hamiltonian ($\hat{H}(t) \Rightarrow \hat{H}_F$)
- Time-dependent Hamiltonian

Photodissociation dynamics of the D₂⁺ molecule



Photodissociation dynamics of the D₂⁺ molecule

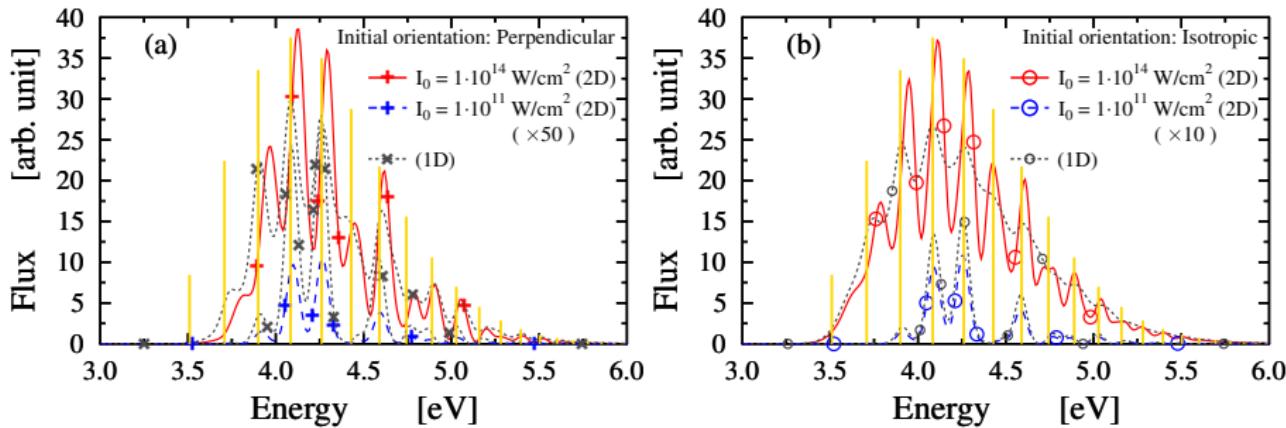


1D and 2D calculations are practically the same. There is no rotation for this initial orientation.

G. J. Halász, Á. Vibók, H.-D. Meyer and L.S. Cederbaum, *J. Phys. Chem. A.* **117**, 8525, (2013).

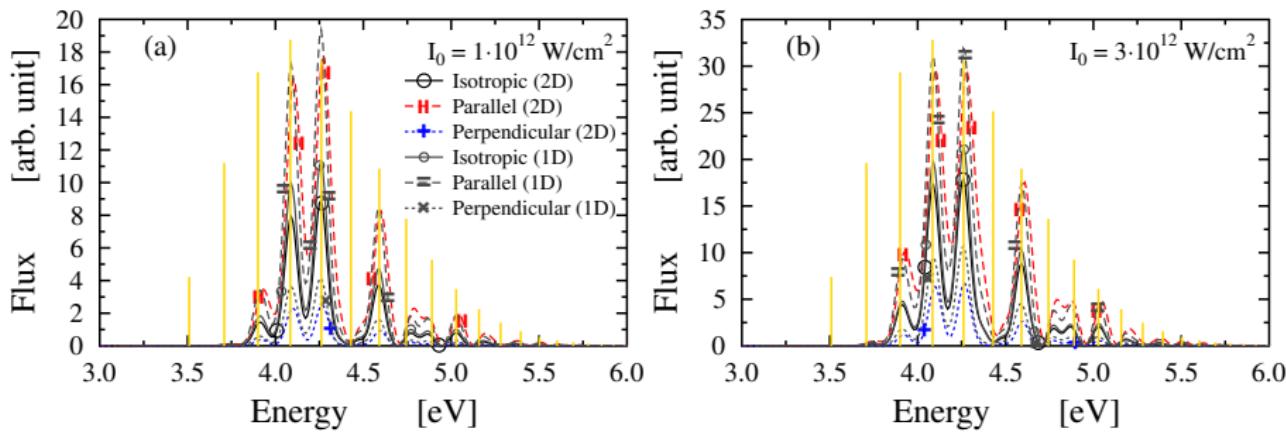
Szeged 2016, november 10.

Photodissociation dynamics of the D₂⁺ molecule



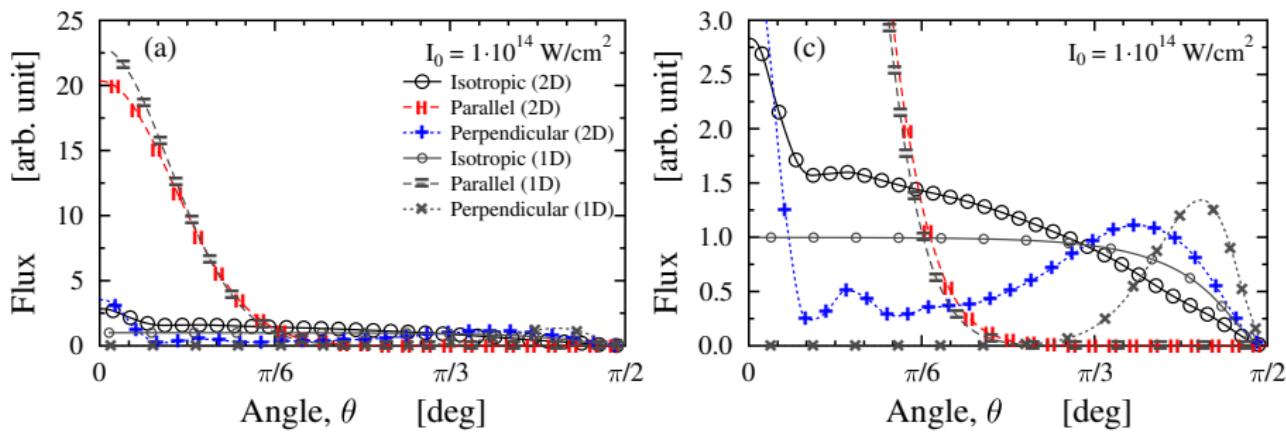
The 1D and 2D results are very different! The rotation has a very significant role for these geometrical arrangements. The dissociation probability is strongly dependent on the initial alignment.

Photodissociation dynamics of the D₂⁺ molecule



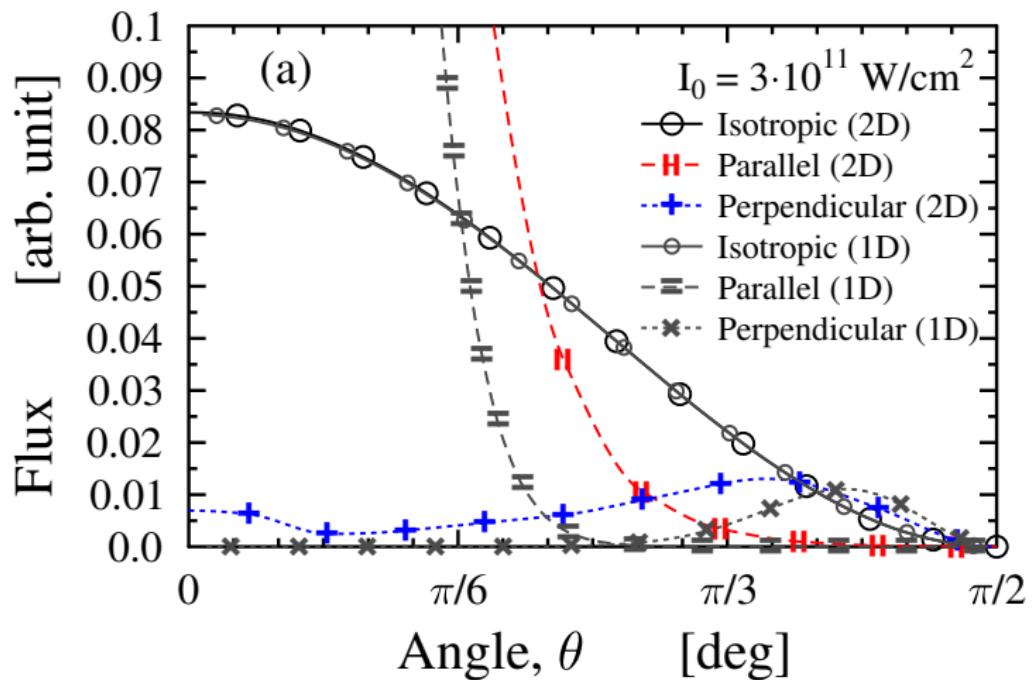
Below the intensity of $1 \times 10^{13} \text{ W/cm}^2$ the dissociation probability of the $\nu = 5$ is practically zero. Fragment energies from this eigenstate are missing in the spectra.

Angular Distribution (FC)



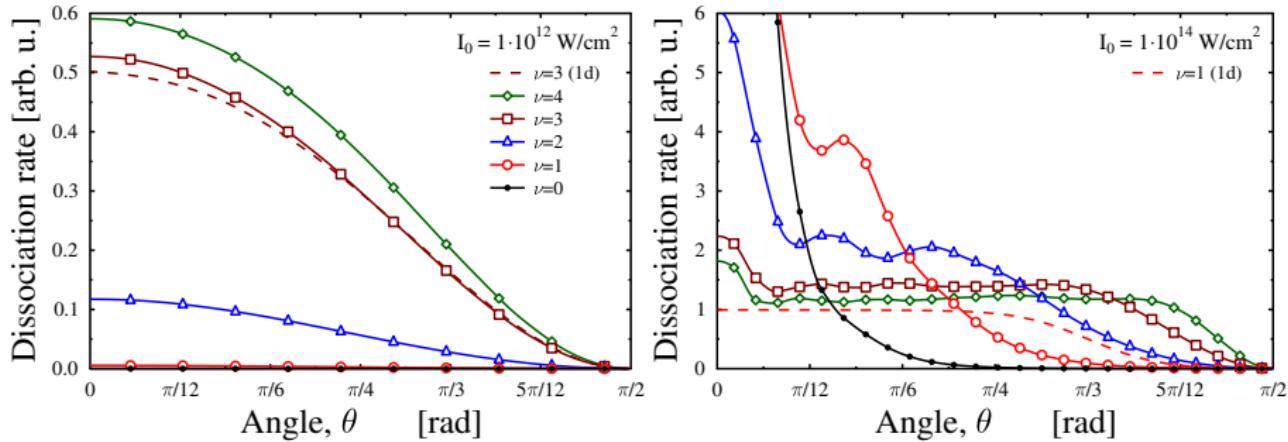
For larger intensities characteristic humped structure in the full 2D curves (isotropic and perpendicular). There are no additional patterns in 1D.

Angular Distribution (FC)



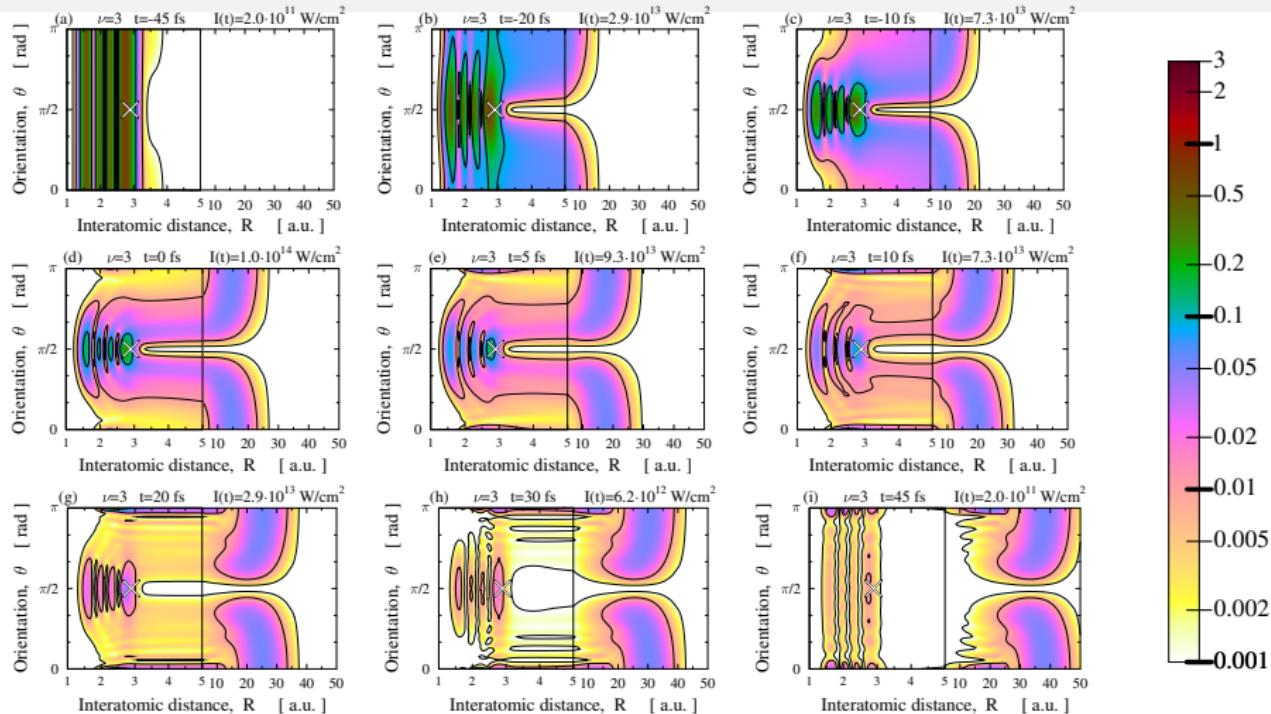
Curves are smooth both for the 1D and 2D calculations.

Angular Distribution (v.e.s.)



Again, curves are smooth for low intensities and bumpy structured for high intensities.

Nuclear Wave packet Density



Snapshots from the real-time evolution of the interference appearing in the angular distribution of the dissociated particles. $I=1 \times 10^{14} \text{ W/cm}^2$ intensity and $\nu = 3$ vibrational state are applied. The cross denotes the position of the LICCI.

G. J. Halász, Á. Vibók, N. Moiseyev and L.S. Cederbaum, *PRA* **88**, 043413, (2013).

Szeged 2016. november 10.

Observation of Quantum Interferences via Light-Induced Conical Intersections in Diatomic Molecules

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We observe energy-dependent angle-resolved diffraction patterns in protons from strong-field dissociation of the molecular hydrogen ion H_2^+ . The interference is a characteristic of dissociation around a laser-induced conical intersection (LICI), which is a point of contact between two surfaces in the dressed two-dimensional Born-Oppenheimer potential energy landscape of a diatomic molecule in a strong laser field. The interference magnitude and angular period depend strongly on the energy difference between the initial state and the LICI, consistent with coherent diffraction around a cone-shaped potential barrier whose width and thickness depend on the relative energy of the initial state and the cone apex. These findings are supported by numerical solutions of the time-dependent Schrödinger equation for similar experimental conditions.

DOI: [10.1103/PhysRevLett.116.143004](https://doi.org/10.1103/PhysRevLett.116.143004)

Kísérlet

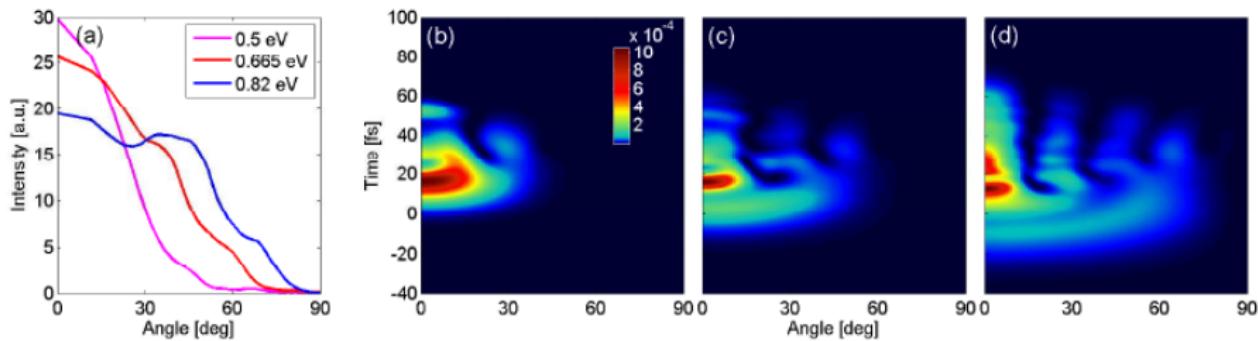
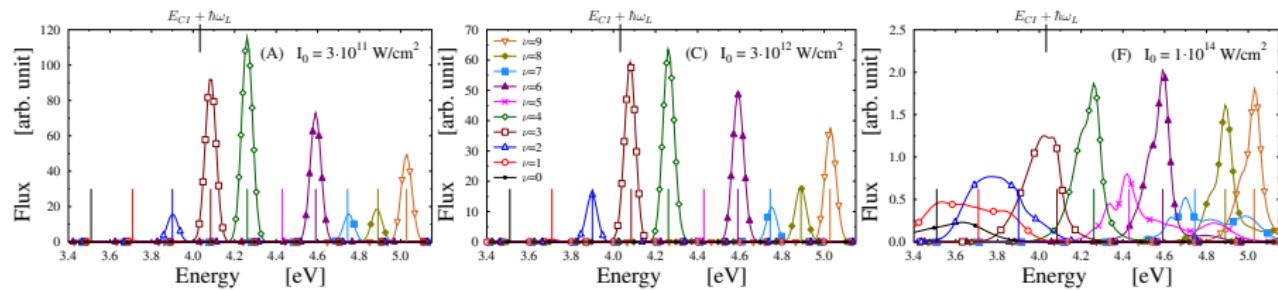


Fig. 1. (a) Measured dissociation yield vs Angle of H_2^+ for kinetic energy release values that correspond to levels $v = 7, 8, 9$ reveal modulations at different angles. (b-d) Calculated disassociation probability as function of time and angle for molecules that were initialized in the (b) $v = 7$, (c) $v = 8$ and (d) $v = 9$ vibrational eigen-states, in the ground rotational state $j = 0$. Peak intensity of pulse happens at $t = 0\text{fs}$.

- ① G. J. Halász, Á. Vibók and L.S. Cederbaum, *J. Phys. Chem. Lett.*, **6**, 348, (2015);
- ② G. J. Halász, Á. Vibók, N. Moiseyev and L. S. Cederbaum, *Phys. Rev. A*, **88**, 043413 (2013);

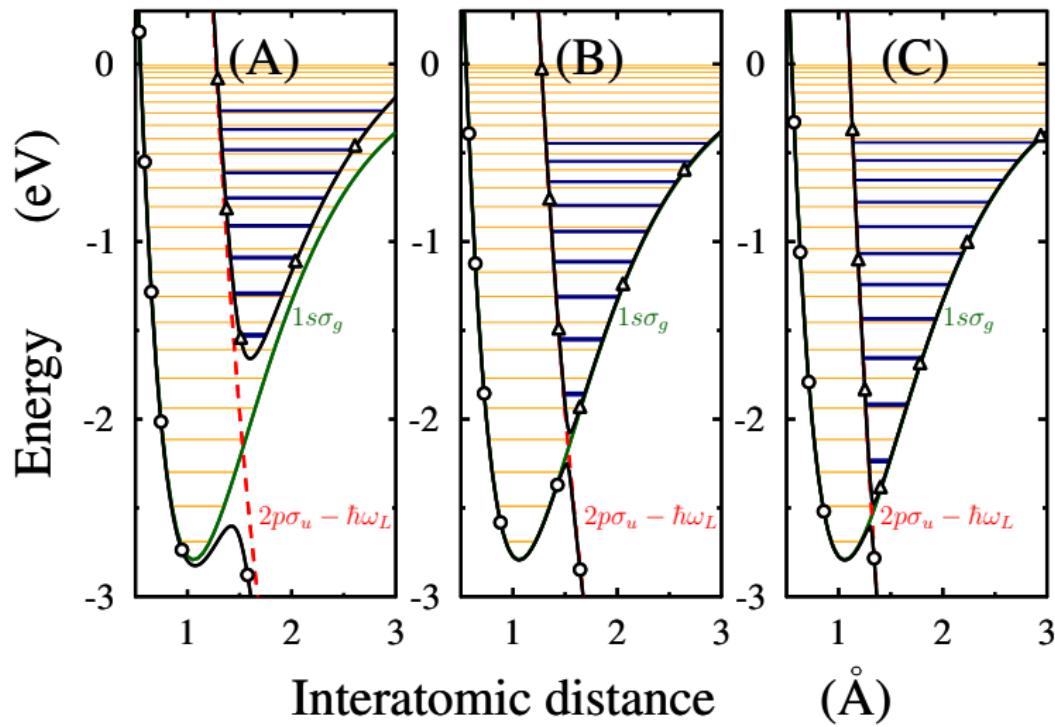
First Direct Result



For lower intensities the dissociation probability from $\nu = 5$ is very small (practically zero). From $\sim 10^{13} \text{ W/cm}^2$ the flux starts to grow, but its value still remains moderate even at the largest 10^{14} W/cm^2 intensity.

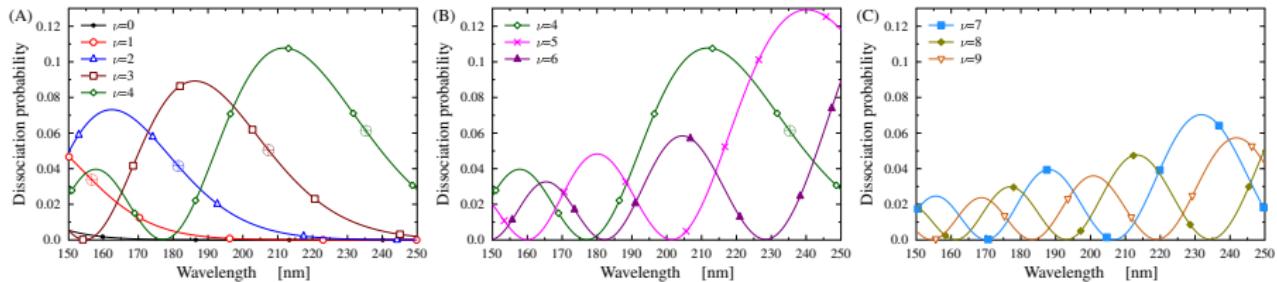
G. J. Halász, A. Csehi, Á. Vibók and L.S. Cederbaum, *J. Phys. Chem. A.* **118**, 11908, (2014).

Upper Adiabatic Potentials (1D)



G. J. Halász, A. Csehi, Á. Vibók and L.S. Cederbaum, *J. Phys. Chem. A.* **118**, 11908, (2014).
Aubanel, E. E.; Gauthier, J. M. and Bandrauk, A. D., *Phys. Rev. A* **48**, 2145-2152, (1993).

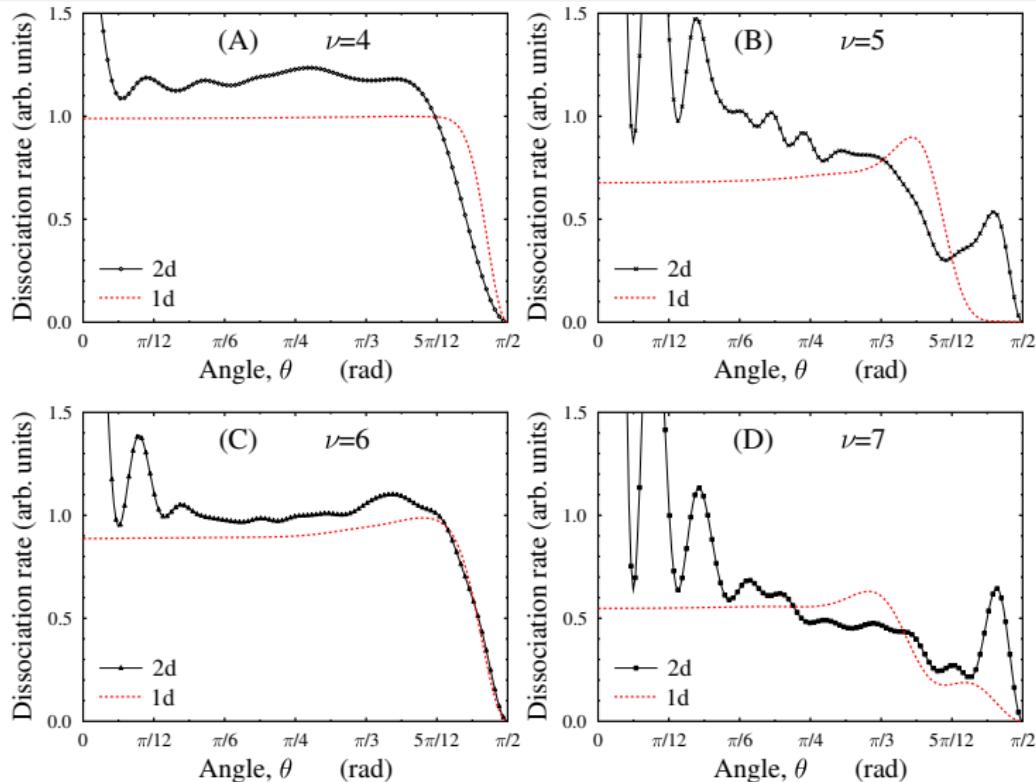
Photodissociation Probability (1D)



Several pairs of wavelengths and vibrational quantum numbers exist in the studied parameter interval for that the values of the flux are close to zero.

G. J. Halász, A. Csehi, Á. Vibók and L.S. Cederbaum, *J. Phys. Chem. A.*, **118**, 11908, (2014).

Angular distribution (V.E.S)



Summary

- ① Diatomic molecules exhibit CIs which are induced by laser waves.
- ② In this case the rotational and vibrational degrees of freedom provide the 2 dimensional branching space.
- ③ These CIs have strong impact on the molecular dynamics, alignment, dissociation probability and could also be strong impact on other physical quantities.
- ④ The energetic position of this CI can be controlled by the laser frequency and the strength of its NACs by the laser intensity.
- ⑤ In polyatomic systems CIs are given by nature and induced by laser light can interplay and will lead to a wealth of new phenomena.

Present and Future

- ① Towards the full dynamical description of D_2^+ in intense laser field.
Dissociation and Ionization of D₂+....
- ② Quantum control with chirped LICL....
- ③ LICL in cavity.....
- ④ LICL in polyatomic molecule.....

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Thank you for your attention!